

HETEROGENEOUS OXYGEN ISOTOPIC COMPOSITION OF A COMPLEX WARK-LOVERING RIM AND THE MARGIN OF A REFRACTORY INCLUSION FROM LEOVILLE. J. I. Simon¹, J. E. P. Matzel², S. B. Simon³, P. K. Weber², L. Grossman³, D. K. Ross^{1,4}, and I. D. Hutcheon². ¹Center for Isotope Cosmochemistry and Geochronology, ARES NASA-JSC, Houston, TX 77058, USA (Justin.I.Simon@NASA.gov), ²LLNL, Livermore, CA 94551, USA, ³The University of Chicago, Chicago, IL 60637, USA, ⁴Jacobs Tech., TX 77058, USA.

Introduction: Wark-Lovering (WL) rims [1] surrounding many refractory inclusions represent marker events in the early evolution of the Solar System in which many inclusions were exposed to changes in pressure [2], temperature [3], and isotopic reservoirs [4-7]. The effects of these events can be complex, not only producing mineralogical variability of WL rims [2], but also leading to mineralogical [8-10] and isotopic [7, 11, 12] changes within inclusion interiors. Extreme oxygen isotopic heterogeneity measured in CAIs has been explained by mixing between distinct oxygen gas reservoirs in the nebula [13]. Some WL rims contain relatively simple mineral layering and/or are isotopically homogeneous [14, 15]. As part of a larger effort to document and understand the modifications observed in some CAIs, an inclusion (L6) with a complex WL rim from Leoville, a member of the reduced CV3 subgroup was studied. Initial study of the textures and mineral chemistry was presented by [16]. Here we present NanoSIMS oxygen isotopic measurements to complement these petrologic observations.

Sample: L6 is a pristine compact Type A (CTA) inclusion with clusters of spinel (typically euhedral, ~50 μm across) and fassaite grains (anhedral) enclosed in visually unaltered melilite that exhibits normal compositional zoning (Åk_{3-30}) within the margin (~200 μm) of the inclusion [16]. At the edge of the inclusion is a nearly continuous and often thick (up to 100 μm) layer of spinel intergrown with the melilite interior. Outside of the main spinel layer are additional layers composed of pyroxene \pm melilite. Based on petrography and mineral chemistry [16], five generations of pyroxene were identified in the WL rim. In the section studied herein, the innermost is Ti-bearing (Ti-pyx) and appears intergrown with the “main” spinel layer. This Ti-pyx ($\leq 10 \mu\text{m}$) becomes less Ti-rich outward and is intergrown with a mixed layer of fine-grained melilite and spinel of varying thickness. Locally the fine-grained melilite layer has a range of grain sizes and can be found in contact with the “main” spinel layer. Coarser melilite tends to enclose less spinel. In places, a second Ti-pyx-melilite layer exists with a distinct Ti-pyx composition from the first [16]. Finally, the entire inclusion and complex rim is surrounded by a uniform layer of diopside (~15 μm), in some places in direct contact with Ti-pyx from an inner layer and sometimes directly

overlying the irregular fine-grained mixed melilite-spinel layer (Fig. 1).

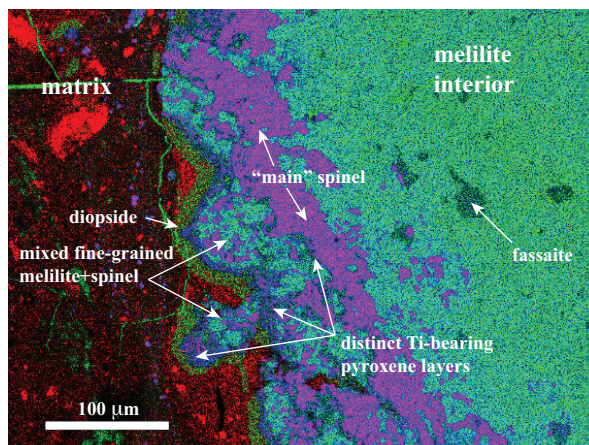


Figure 1. Mg (red), Ca (green), Al (blue) X-ray image of L6 exhibiting a “simple” example of the Wark-Lovering rim stratigraphy surrounding the inclusion.

Methods: We used the LLNL NanoSIMS 50 to perform oxygen isotopic measurements following published methods [7]. Data come from multiple traverses across the rims and outer margin of the interior of L6 to define oxygen isotopic zoning profiles. Data points are ~2 μm diameter single-phase analyses as evaluated by their $^{28}\text{Si}/^{16}\text{O}$ ion ratios and SEM imagery after the NanoSIMS measurements. Oxygen isotope compositions are reported as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$, which represents the departure from the terrestrial mass fractionation (TMF) line that defines the terrestrial oxygen reservoir. Based on standard analyses, the precision is <3‰/amu (2σ). We evaluated instrumental mass fractionation (IMF) and reproducibility by repeat analyses of spinel, anorthite, grossular, pyroxene, and forsterite standards. The difference in $\Delta^{17}\text{O}$ among the terrestrial standard minerals was similar to our typical uncertainty (~3.0‰). Mineral compositions, and X-ray and backscattered electron maps were used to guide NanoSIMS traverses and verify the mineralogy of analysis spots.

Results: Oxygen isotope data come from traverses spanning the WL rims and/or margin of the interior (Fig. 2). Like several CAIs studied previously [7, 17, 18], L6 exhibits large variations in $\Delta^{17}\text{O}$ (>20‰). Compared to the inclusion reported by [7], interior melilite in L6 is more homogeneous and ^{16}O -poor ($\Delta^{17}\text{O} \sim -6\text{‰}$). The exception is a systematic $\Delta^{17}\text{O}$ de-

crease from $\sim -6\%$ to -22% at the edge. Spinels in the “main” layer at the margin are ^{16}O -rich ($\Delta^{17}\text{O} \leq -25\%$). The Ti-pyx layers have intermediate $\Delta^{17}\text{O}$ compositions ($\Delta^{17}\text{O} \sim -14$ to -18%). Melilite from the mixed layer exhibits extreme oxygen isotopic heterogeneity with $\Delta^{17}\text{O}$ values ranging from $\sim -6\%$, like a majority of the interior crystals, to -27% in one melilite. Diopside in the outermost layer exhibits less variability with $\Delta^{17}\text{O}$ from -15% to -23% .

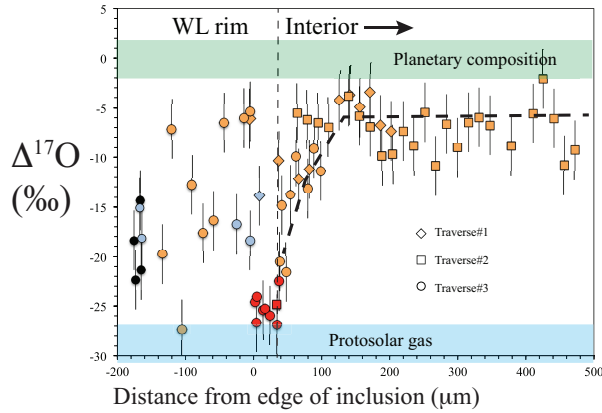


Figure 2. Oxygen isotopic zoning across the Wark-Lovering rim layers and melilite margin of L6 obtained by NanoSIMS. Individual traverses are identified by symbol; melilite analyses are tan, spinel red, Ti-pyx blue, and diopside black. Thick dashed curve emphasizes the oxygen isotopic zoning in melilite at the margin of L6. Spinel and the most ^{16}O -rich rim melilite match the oxygen isotope composition of [19] and likely represent the protosolar composition.

Discussion: The fine-scale spatial zoning and textural features create concern if the mineral analyses represent pure phases. A quantitative means to evaluate this possibility is shown in Fig. 3 where we plot the $^{28}\text{Si}/^{16}\text{O}^-$ secondary ion ratio versus distance for the data shown in Fig. 2; data are not corrected for differences in ion yield. If the ^{16}O -rich composition of melilite was due to overlap of the primary beam onto spinel, the $^{28}\text{Si}/^{16}\text{O}^-$ ratio would show marked changes from the ~ 0.02 value consistent with pure melilite.

Oxygen isotope compositions within the interior and compositional zoning at the margin of L6 show great similarity to a previously studied CAI (Ef-1), a CTA from Efremovka [17]. The WL rim on L6 is much more complicated (both mineralogically and isotopically). The oxygen isotopic compositions of the WL rim phases share some similarity to previously studied WL rims [7, 17], e.g., spinel is generally ^{16}O -rich while pyroxene has intermediate $\Delta^{17}\text{O}$ values. The wealth of melilite data from a WL rim is new, as is the extreme O-isotope heterogeneity. Three Ti-pyx layers seen in [16] appear to have similar oxygen isotopic compositions to one another, indicating that there were

more cycles of deposition than recorded by isotopic differences. The average diopside $\Delta^{17}\text{O}$ value is slightly more ^{16}O -rich than the average Ti-pyx value (from any or all inner Ti-pyx layers). Likewise, melilite in the WL-rim exhibits a general inward trend towards ^{16}O -poor values despite the existence of ^{16}O -rich melilite at the edge of the inclusion. Although it is assumed that the inclusion formed from an ^{16}O -rich protosolar gas [19], the general sense of zoning in the WL-rim, as well as the zoning in melilite at the margin of the inclusion, suggest that the inclusion progressively exchanged or formed from ^{16}O -poor and then ^{16}O -rich reservoirs. The heterogeneity within the interior supports our previous conclusion that CAIs record a progressive trend in the extent of exchange with a number of isotopically distinct reservoirs that is decoupled from mineralogical evidence of secondary alteration [17]. The WL rim and interior data support models in which CAIs were transported between at least two distinct nebular gases multiple times, e.g., [7].

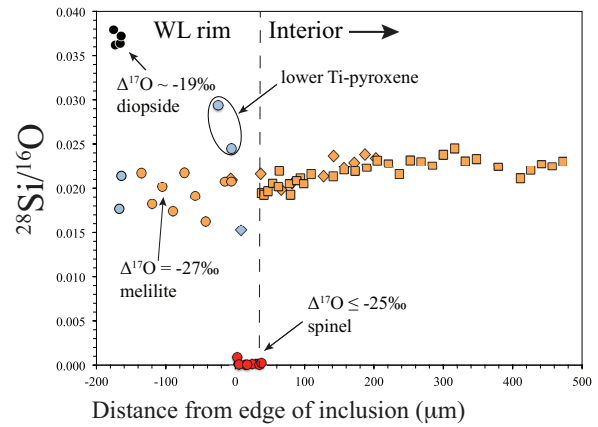


Figure 3. $^{28}\text{Si}/^{16}\text{O}$ ion ratio profile across the minerals in the Wark-Lovering rim layers and interior of L6 used to identify data that could come from analytical mixtures. Spurious data are not shown (see text). Shifts in $^{28}\text{Si}/^{16}\text{O}$ among melilite and between innermost high Ti-pyx, lower Ti-pyx, and diopside, combined with $\Delta^{17}\text{O}$ indicate negligible contamination from spinel and are those generally expected from their chemical compositions. Symbols are as in Fig. 2.

- References:** [1] Wark, D.A. and J.F. Lovering (1977) *PLSC*, 95-112. [2] Simon, J.I. et al. (2005) *EPSL*, 238, 272-283. [3] Young, E.D. et al. (2005) *Science*, 308, 223-227. [4] Yurimoto, H. et al. (1998) *Science*, 282, 1874-1876. [5] Krot, A.N. et al. (2002) *Science*, 295, 1051-1054. [6] Aleon, J. et al. (2007) *EPSL* 263, 114-127. [7] Simon J.I. et al. (2011) *Science*, 2011, 1175-1178. [8] Keller, L.P. and P.R. Buseck (1991) *Science*, 1991, 252, 947-949. [9] Metzler, K., A. et al. (1992) *GCA*, 56, 2873-2897. [10] Jacobsen, B. et al. (2011) *ApJL*, 2011, 731(L28). [11] Fagan, T.J. et al. (2004) *MPS*, 39, 1257-1272. [12] Simon, J.I. and E.D. Young (2011) *EPSL*, 304, 468-482. [13] Clayton, R.N. et al. (1977) *EPSL*, 34, 209-224. [14] Matzel, J.E.P. et al. (2013) *LPSC* Abst. #2632. [15] Bodénan, J.-D. et al. (2013) *Metsoc* Abst. #5187. [16] Simon, S.B. and L. Grossman (2013) *LPSC* Abst. #2793. [17] Simon, J.I. et al. (2012) *LPSC* Abst. #1340. [18] Simon, J.I. et al. (2013) *LPSC* Abst. #1828. [19] McKeegan, K.D. et al. (2011) *Science*, 332, 1528-1532.